

Preventing Hydrogen Sulfide Formation in Shipboard AFFF Fire Protection Systems

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ABSTRACT

There is a very serious problem aboard U.S. Navy ships from generation of toxic hydrogen sulfide (H_2S) in Aqueous Film Forming Foam (AFFF) solutions used for shipboard fire protection. This is the result of the action of sulfate reducing bacteria (SRB) in mixtures of seawater and AFFF, which remain stagnant for significant time periods in shipboard fire protection system piping. Over time, microbes present in seawater consume organic materials in the AFFF mixture and can deplete the dissolved oxygen. If the reduction-oxidation potential falls low enough, anaerobic action of the SRB on the sulfate present in seawater can then result in H_2S generation, reaching dangerous levels. The recommended ceiling for exposure to hydrogen sulfide is only 10 ppm.

If the microbes causing oxygen depletion and / or the sulfate reducing bacteria can be eliminated (or sufficiently minimized), the dangerous generation of H_2S would not occur. The Navy Technology Center for Safety and Survivability is participating in a research project for the Naval Sea Systems Command (NAVSEA) to evaluate several treatment modalities for their ability to inhibit hydrogen sulfide formation in AFFF/seawater mixtures and for possible deleterious effects on AFFF performance. Various approaches have been considered employing laboratory evaluations (dynamic surface tension and Ross-Miles foamability), and 28 ft² pool fire extinguishment and burnback protection field tests (Military Standard MIL-F-24385F). The protocol selected for NAVSEA shipboard H_2S generation mitigation testing is a combination of a commercial broad spectrum biocide with a molybdenum compound which is a specific inhibitor of SRB.

INTRODUCTION

Aqueous Film Forming Foam (AFFF) was developed over forty years ago by the Naval Research Laboratory (NRL) together with 3M to respond to aircraft carrier fires that unfortunately resulted in major loss of life, as well as equipment. (Tuve, Peterson, Jablonski, and Neill, 1964). The protein foams in use at that time were not able to protect against very large flammable liquid spill fires, especially in the rapid time scale required to keep fire-exposed ordnance from detonating. The use of fluorosurfactants allowed the foams to form a stable thin liquid film on top of less dense hydrocarbon liquids, with the foam ‘floating’ on the film. This “Light Water” provided an extinguishing agent with self-sealing and spreading properties to greatly enhance its protection performance. Film forming fluorosurfactant fire fighting foams are now used world-wide to provide protection against two dimensional flammable liquid fires, for many land-based applications in addition to shipboard usage.

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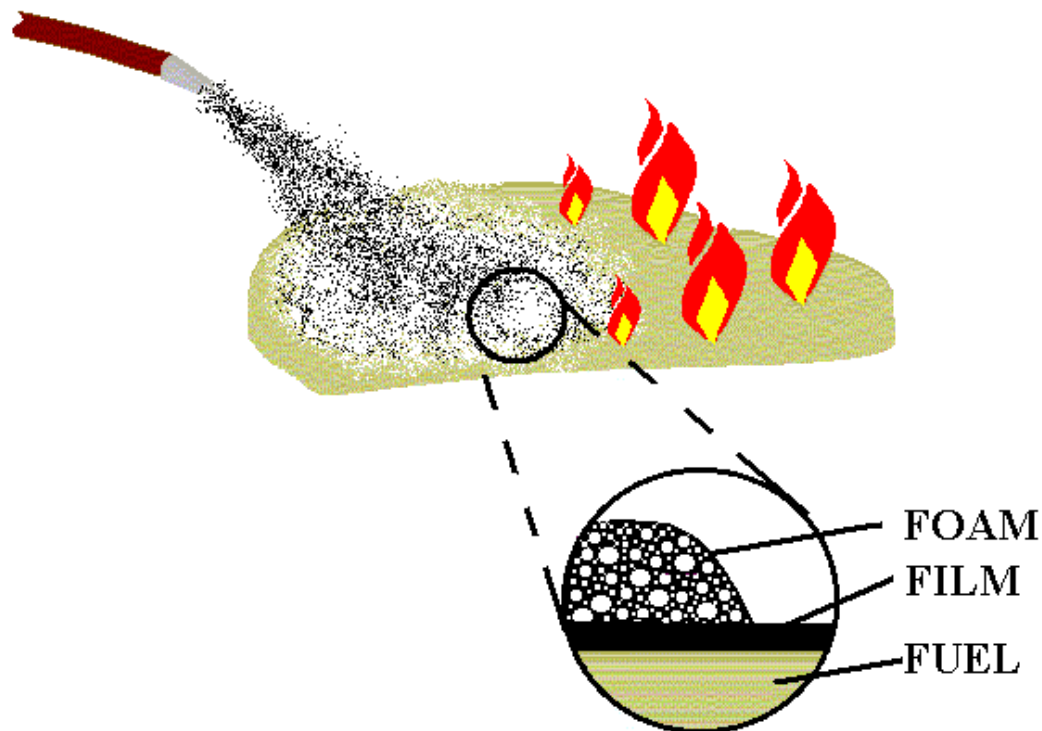


Figure 1: Schematic of structure of AFFF foam and film layers on water

AFFF is used in the U.S. military, and in most civilian applications worldwide, as either a “3%” or a “6%” concentrate, alternately referred to as Type 3 or Type 6, respectively. The numbers refer to the percentage of foam concentrate mixed with either fresh water or seawater (e.g. a “6%” AFFF concentrate is nominally used as a mixture of 6% concentrate and 94% water). In the U.S. DoD, the 6% concentrate is used in most shipboard applications, while 3% is used in most land-based applications. A 1% AFFF concentrate is sold by some manufacturers for civilian uses, but is not at present included in the MilSpec. The discharge nozzle can either be handheld, or in cases such as the flight decks of aircraft carriers, built into the ship.

A number of environmental issues have come under more careful consideration in recent years and may impact AFFF usage (Williams and Sheinson, 2003). The concern that is the subject of this work is the generation of hydrogen sulfide (H_2S) when organic rich AFFF remains mixed with natural seawater for long time periods in a non-aerated environment. H_2S , causing the familiar odor of rotten eggs, is a toxic gas at higher concentrations. It is particularly insidious as one acclimates to its odor and might not realize dangerous levels are present.

AFFF for US Navy shipboard fire protection use is generated by mixing the concentrate with seawater as needed. The AFFF-seawater mixture remains in the piping after system use, as the system always remains charged for rapid response. The time interval may be months, and pipe runs on some ship classes can contain hundreds of gallons. Under these conditions, microbes always present in seawater may consume the organic materials in the AFFF mixture and deplete the oxygen originally dissolved in the stagnant AFFF/seawater mixture. If the reduction-oxidation potential falls low enough, anaerobic sulfate reducing bacteria (SRB) will

use the sulfate present in seawater as an oxygen source to metabolize organic components of the AFFF, producing sulfide as a by-product. This can then result in H₂S generation reaching dangerous levels. A lesser concern related to microbial activity is 'scaling,' i.e., biofouling, of piping (a potentially serious issue for titanium piping, including fire mains, in future ships).

H₂S MITIGATION APPROACHES

The formation of hydrogen sulfide in AFFF systems is the result of a sequence of events involving several necessary factors. These in turn suggest possible approaches to interrupt the sequence and prevent H₂S formation.

For H₂S to form, the following conditions are needed:

1. There must be both organic material which can be metabolized by bacteria in sufficient quantity to deplete the available dissolved oxygen, and a source of sulfate.

AFFF contains organic components, which are necessary to achieve the necessary foam quantity and performance. About 10% of the dissolved salts in seawater are sulfates (some AFFF formulations contain sulfate also, but their contributions to the total sulfate load in the seawater/AFFF mixture are minor compared to that of the seawater). Reducing the concentrations of organics or sulfate in the AFFF/seawater mixture is not practical.

2. The dissolved oxygen in the seawater must be depleted by aerobic bacteria metabolism, so that anaerobic conditions conducive to SRB exist.

The SRB do not function until anaerobic conditions exist. If the aerobic bacteria population in seawater could be killed or greatly decreased, anaerobic conditions in the piping will be avoided or minimized. Attacking the microbe population can be accomplished via oxidizing and non-oxidizing biocides, ultraviolet (UV) radiation and other modalities. There are practical difficulties getting sufficient UV intensity through seawater, which contains organics and scattering particles. Special windows would also be required. Thus, use of biocides to control aerobic bacteria and prevent the formation of anaerobic conditions is the approach which we chose to pursue.

3. There must be no aeration of the mixture or alternative oxidant sources.

Aeration or adding materials to maintain the redox potential over time is a possible approach. However, it would likely require significant engineering modifications on existing shipboard installations, and was not explored further under this task.

4. SRB must be able to live in the anaerobic environment, and sulfide they produce must exceed the solubility limit and undergo no chemical reactions to be released as hydrogen sulfide gas.

The functioning of the SRB could be targeted by biocides specific to SRB, or sulfide itself might be able to be scavenged chemically. One of these approaches could be a second line of defense after attempting to control the growth of aerobic bacteria.

Complicating the implementation of an approach are the tendencies of bacteria to colonize and form biofilms including on pipe surfaces, crevices and accumulated debris. Bacteria in such protected environments will be more difficult to eliminate. Continued or periodic subsequent treatment with provision for circulation may be necessary, but are beyond the scope of this effort, which was to identify approaches that would not negatively affect AFFF performance.

SELECTION OF BIOCIDES

The commercial fire fighting foam sector has dealt with and handled microbial degradation in other types of foam concentrates. The threat facing the commercial products from microbial growth is much worse for the class of Alcohol Resistant (AR) foams, for which there is no military specification. In order to be able to maintain foam in the presence of alcohols, which can serve as foam breakers, the typical AR formulation is 'built up' with organic materials, typically polysaccharides. These materials serve as nutrients for many microorganisms, making the foams much more supportive for microbial life. Therefore AR-AFFFs tend to be very prone to bacterial contamination and degradation. As a result, AR-AFFFs typically contain biocides designed to protect the (unmixed) concentrate from degradation.

In order to make use of AFFF manufacturers' experience and ideas regarding inhibition of bacterial growth, we contacted all the manufacturers with AFFF products on the Qualified Procurement List (QPL, signifying certification of the product's compliance with Military Standard MIL-F-24385F). In the course of these contacts, the manufacturers gave information on controlling bacterial growth in AR-AFFF concentrates, which contain high levels of nutrients. Thus the adaptation of the methods used to control bacteria in AR-AFFF concentrates to controlling bacteria in AFFF/seawater mixtures was identified as a promising approach.

For AR-AFFFs, the biocide is intended to prevent bacterial degradation of the undiluted concentrate. After dilution, there is always an issue of bacterial attack of the foam mixture. The implication, mentioned by some of the manufacturers, is that higher antimicrobial concentrations would likely be needed to provide long-term protection for seawater/AFFF mixtures in shipboard piping.

All the manufacturers felt that bleach (hypochlorite), used as a disinfectant to control bacterial growth (including as an approach to prevent hydrogen sulfide formation), would adversely interact with their products and degrade performance. It was felt hypochlorite might react with both glycol ethers such as butyl carbitol (used as foam extenders in AFFF) and the surfactants in AFFF, particularly during an extended period of storage. Instead, antimicrobial chemicals were suggested and are employed by the industry to control bacterial growth in their products.

A biocide used to control aerobic bacteria for this application must have long-duration effectiveness, have broad spectrum effectiveness against many different organisms, be effective at neutral and slightly alkaline pH, and have minimal environmental persistence, reasonable toxicity for personnel safety, and approval for use in non-potable water systems.

After consideration of a variety of biocides, the class which appeared most promising, and was selected for further testing, was that of polycyclic amines. Examples of this class include Dowicil 75 (manufactured by Dow Chemical) and Busan 1024 (manufactured by Buckman Labs, Memphis). Both of these compounds were suggested by foam manufacturers, and are used in AR-AFFF formulations to prevent bacterial growth. This prior use in foam formulations suggests that these biocides are unlikely to interfere with AFFF performance.

Biocides in this class are slowly hydrolyzed by water, eventually producing formaldehyde, which is the main anti-bacterial active ingredient. Since the active material is only produced after hydrolysis, handling of the parent compound poses less risk to personnel. Also, formaldehyde has a fairly short lifetime in the environment, avoiding the problems of using an environmentally-persistent toxin.

A number of other types of biocides also work by degradation to produce formaldehyde. In some cases the rate of hydrolysis is very high, meaning the biocide is intended to be used as a short-term “shock treatment” to kill bacteria, rather than protection over an extended time period. In other cases, the rate of hydrolysis is dependent on pH, and the biocides will not give a consistent behavior over the pH range (roughly 6-9) likely to be encountered in shipboard seawater/AFFF mixtures.

We feel that while the same concentrations of antimicrobial in the diluted water-AFFF mixture that is used in the commercial foam concentrate would achieve effectiveness for controlling bacteria in the liquid mix, further increased factors (at least by 10x if not 100x) would be required to combat the higher bacteria concentrations from seawater especially those microorganisms in biofilms. If a continued effective presence of antimicrobial can be maintained, it may not be necessary to dose for destroying biofilms protected microbes.

Development of resistance is a potential concern. It may be unlikely that any one biocide will provide a long-term solution. Not all bacteria will be equally susceptible to the compounds and cells may develop resistance over time. A strategy for long-term control may need to include switching biocides periodically.

EXPERIMENTAL APPROACHES

Whatever means is employed to address H₂S generation must not cause a significant decrease in AFFF fire protection capability. Thus, this task focused on literature research to identify mitigation approaches, evaluation of their impact on AFFF properties via laboratory screening evaluations (surface tension and foaming properties), and fire performance field evaluations. Foam film capability to float on less dense flammable liquids depends on adequate reduction of surface tension. Foam must maintain itself without draining (breaking down) too quickly. And most importantly, the modalities performing the most satisfactorily in the laboratory screening evaluations must not show unsatisfactory results in field fire tests.

Two laboratory tests were employed to give an initial evaluation of the effect of various antimicrobial additives on AFFF properties. One was an evaluation of foaming using the Ross-Miles foaming protocol. This protocol, which is widely used in evaluation of foaming properties

but differs from the MIL-F-24385F test, measures the amount of foam generated, its water content, and persistence, by a gravity-feed of liquid into a receptacle. None of the additives tested caused a noticeable difference in the foaming properties of any of the AFFF formulations according to the Ross-Miles test.

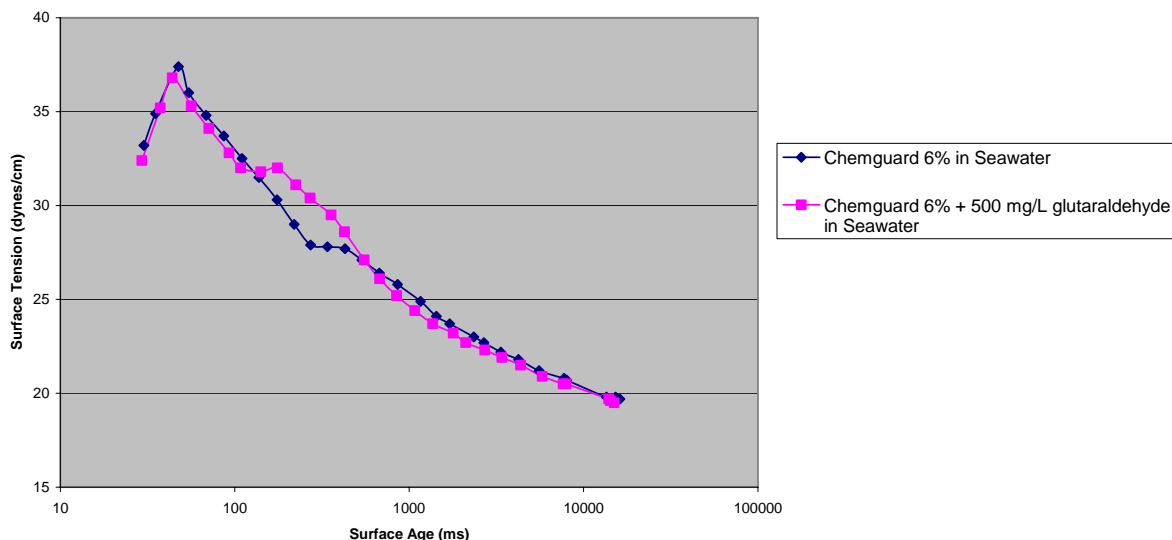


Figure 2: Dynamic surface tension curves of Chemguard AFFF with and without addition of glutaraldehyde.

The effect of the additives on surfactant performance was studied by recording the dynamic surface tension (DST) of the additive/AFFF combination. Dynamic surface tension measures not only the amount by which the surfactant reduces surface tension, but the speed at which it does so by forming a surface monolayer.

DST was measured by a bubble-pressure tensiometer (Kruss) which measures the overpressure necessary to create a bubble from an orifice, which is determined by the surface tension. By varying the bubbling rate, the speed at which the surfactant acts can be determined. A plot of dynamic surface tension vs. surface age gives a monotonically decreasing line, which asymptotically approaches the equilibrium surface tension as the surface age becomes large. An undesirable effect of an additive on the surfactants' performance is indicated by an increase in the asymptotic value of surface tension, and/or a decrease in the rate at which the equilibrium is approached. Figure 2 shows AFFF DST curves with and without glutaraldehyde added. The two curves are very similar, indicating no significant effect of glutaraldehyde on surfactant behavior.

It is likely the very significant load of oxidizable material in the mixture (AFFF hydrocarbon surfactants and solvents, seawater organic contents) will make sustaining a residual effectiveness very difficult. Additional application to provide continued control would likely to be required. Evaluations with hypochlorite (bleach, commonly used a swimming pool disinfectant) showed that even very significant concentrations of the added oxidizing chemical were quickly reacted, with no residual presence, and thus, no residual protection. There was also a significant increase in surface tension (Figure 3), which would mean decreased performance. Oxidizing disinfectants, including similar bromine based chemicals, were not considered further.

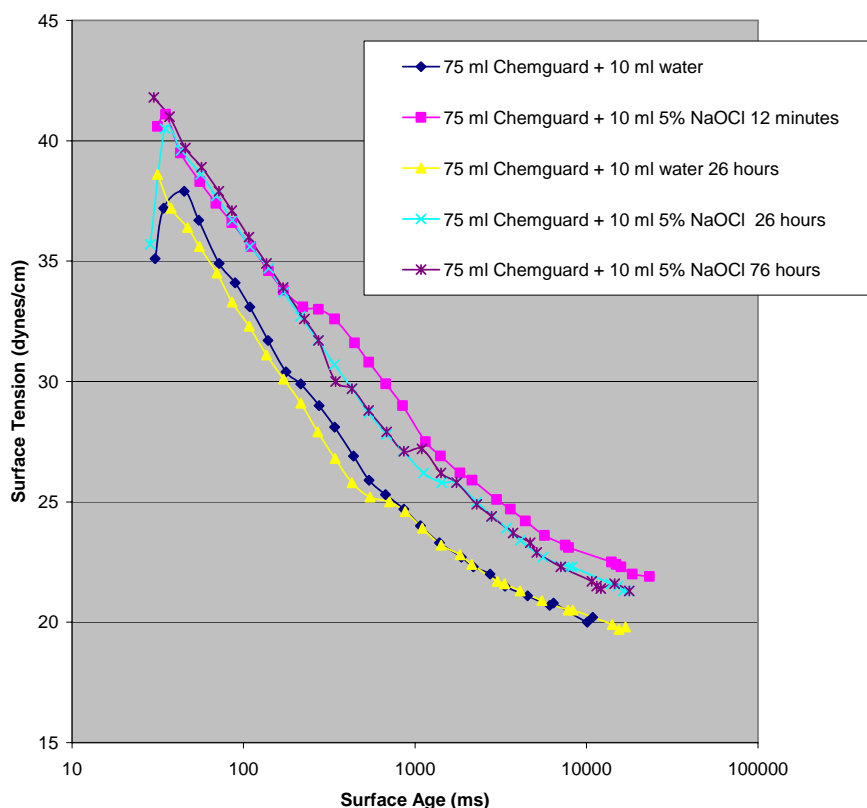


Figure 3: Dynamic surface tension curved of Chemguard AFFF with and without addition of sodium hypochlorite. The higher values of the surface tension when the hypochlorite is added indicate a decrease in the performance of the surfactants.

Glutaraldehyde is widely used as a non-oxidizing sterilizing agent. However, it also proved to be rapidly consumed, leaving no residual protection, and generating a precipitate. For these reasons, and other handling concerns, it was not considered further. Anaerobic sulfate reducing bacteria (SRB) in the AFFF system can be attacked directly with molybdate. Molybdate is not a general antimicrobial but as is chemically similar to sulfate, it is taken up by the SRB. But the SRB are not able to process it, and it interferes with their viability. If addition of molybdate is employed, it may be necessary to provide additions over time.

Dowacil antimicrobial agents were further evaluated in the laboratory, as were molybdate additives. Neither of these additives had a deleterious effect on dynamic surface tension, and both were judged worthy of further investigation, including fire protection performance testing.

FIRE PROTECTION PERFORMANCE

Adducts must not cause significant decrement in fire fighting performance. Therefore we carried out field tests of AFFF fire suppression performance using the MilSpec 28 ft² pool test at the NRL fire test facility in Chesapeake Beach, MD for 10 different mixtures of the four Type 6 QPL AFFFs, without and with adducts. They were mixed in natural seawater (from 12 miles off Norfolk, VA) with accelerated aging at 65 degrees C for ten days as per MIL-F-24385F protocol. Laboratory measurements were also performed to determine the dynamic surface tension (DST)

of the aged mixtures. The sample mixture parameters are listed below in Table 1. All AFFF formulations investigated were Type 6 (intended for use as a 6% mix). The fire suppression tests were all “half-strength” tests, mixed at 3% as opposed to 6% concentration, as that test condition is more challenging and more discriminating for contrasting performance. Using salt water instead of potable water and accelerated aging conditions likewise were chosen to evaluate a more challenging scenario to provide a conservative performance evaluation. Salt water also represented the shipboard conditions. Note that this more severe testing protocol is not part of the MilSpec qualification criteria testing matrix. The purpose was not certification, but testing for performance differences without and with additives.

TABLE 1: Mixtures Used for Accelerated Aging Tests

Sample Number	AFFF Brand	AFFF Concentration	Adduct	Adduct Concentration	Aging at 65 deg C
1	National	3%	None	None	10 days
2	National	3%	Molybdate	5000 mg/L	10 days
3	National	3%	Dowicil 75	2700 mg/L	10 days
4	National	3%	Molybdate Dowicil 75	500 mg/L 2700 mg/L	10 days
5	3M	3%	None	None	10 days
6	3M	3%	Molybdate Dowicil 75	500 mg/L 2700 mg/L	10 days
7	Ansul	3%	None	None	10 days
8	Ansul	3%	Molybdate Dowicil 75	500 mg/L 2700 mg/L	10 days
9	Chemguard	3%	None	None	10 days
10	Chemguard	3%	Molybdate Dowicil 75	500 mg/L 2700 mg/L	10 days

Figure 4 shows the AFFF solutions before oven aging. Although none of the solutions had a noticeable color, the solutions varied considerably in turbidity. The National and especially the 3M AFFF solutions were the cloudiest.



Figure 4. AFFF Solutions before Oven Aging. From left to right: 3M, Ansulite, Chemguard, and National.

Figure 5 shows the AFFF solutions after oven aging for 10 days at 65 degrees Centigrade. Notice that all of the solutions containing Dowicil 75 have a yellowish color. National solutions are still cloudy, along with 3M solutions.



Figure 5. AFFF Solutions after Oven Aging for 10 Days. First row, from left to right: Sample 1, 2, 3, and 4 (National Foam). Second row, from left to right: Sample 5, 6, (3M); 7, 8 (Ansul); 9, 10 (Chemguard). The samples with the yellow-green color (3, 4, 6, 8, and 10) contain Dowicil.

SURFACE TENSION RESULTS

Dynamic surface tension (DST) was measured with a Kruss BP-2 maximum bubble pressure tensiometer. This instrument allows determination of the short-time rate at which the AFFF components lower the surface tension of water. The instrument gives a set of data of surface tension vs. surface age, with the surface tension gradually decreasing as the surface age increases. At large values of surface age (10 seconds or more) the value of the DST approaches the value of static surface tension determined by a ring tensiometer. Tensiometry was performed on all samples used in the field fire performance tests, as well as mixtures of the four AFFF formulations at 3% and 6% (half-strength and full-strength) in artificial (as opposed to natural) seawater. Unlike the natural seawater samples used in the fire testing, the artificial seawater samples were not aged at an elevated temperature.

At lower values of surface age (≈ 100 ms), an unusual effect was noted in the 3M AFFF. The samples aged in natural seawater had surface tension values approximately 10 dynes/cm lower than the samples prepared in artificial seawater. This behavior, not seen with any of the other AFFFs investigated, was not explored further as outside the scope of this task. Dynamic

surface tension at low surface age is important in foam formation. The quasi-equilibrium value (high surface ages—10 seconds in this case) is of more interest for predicting stable film formation and self-sealing behavior, also important in fire fighting performance. If the surface tension of the AFFF is greater than about 22 dynes/cm, it is unlikely to retain film-forming ability on gasoline. Measured values are given below:

Dynamic Surface Tensions (dynes/cm) at surface age of 10 seconds

All Type 6 AFFF mixed at concentrations indicated (6% = full strength; 3% = half strength)

3M: Some degradation going from full strength to half strength, but still better or equal to full strength of other formulations. No significant effect at 10 seconds of natural seawater, aging, or adduct treatment.

3M @6% Artificial Seawater	18.8
3M @3% Artificial Seawater	19.5
3M @3% Natural Seawater aged #5	19.7
3M @3% Natural Seawater+molybdate (.5 g/l) /Dowicil aged #6	19.8

Chemguard: Some degradation going from full strength to half strength. Control in natural seawater not degraded with aging. Some degradation of natural seawater formulation aged with adducts, but still lower surface tension than all Ansul and National half strength mixtures.

Chemguard @6% Artificial Seawater	19.8
Chemguard @3% Artificial Seawater	20.7
Chemguard @3% Natural Seawater aged #9	20.5
Chemguard @3% Natural Seawater+molybdate (.5 g/l) /Dowicil aged #10	21.5

Ansul: Some degradation going from full strength to half strength.

Ansul aged half strength natural seawater close to (bit better, probably not significant difference) to artificial seawater; significant surface tension increase with adducts.

Ansul @6% Artificial Seawater	21.4
Ansul @3% Artificial Seawater	22.4
Ansul @3% Natural Seawater aged #7	22.0
Ansul @3% Natural Seawater+molybdate (.5 g/l) /Dowicil aged #8	24.2

National: Degraded going from full strength to half strength. Very significant degradation of control and all adduct mixtures aged in natural seawater.

National @6% Artificial Seawater	20.8
National @3% Artificial Seawater	22.4
National @3% Natural Seawater aged	28.0
National @3% Natural Seawater+Dowicil aged	28.8
National @3% Natural Seawater +molybdate (5 g/l) aged	28.6
National @3% Natural Seawater +molybdate (.5 g/l) /Dowicil aged	29.3

All the MilSpec QPL Type 6 AFFF mixtures evaluated demonstrated some degradation in surface tension reduction going from full strength @6% to half strength @3% (artificial sea water, not higher temperature aged). This change was least for 3M, increasing slightly through Chemguard and Ansul, and greatest with National AFFF.

3M: Lowest surface tension of all formulations, for all mixture conditions. No significant differences between artificial or natural seawater, aged or not, adducts or not.

Chemguard: No significant differences between artificial or natural seawater, aged or not. Slight dynamic tension increase with adducts. Lower surface tension than Ansul and National formulations.

Ansul: Significant surface tension increase with addition of adducts.

National: Very significant difference (surface tension increases) upon aging when mixed with natural seawater without adducts, somewhat worse with adducts.

Accelerated aging tests were previously performed with 0.5 g/l glutaraldehyde adduct on the four Type 6 QPL certified AFFFs at full strength in artificial seawater, using the same aging protocol. These tests were focused primarily on the stability of glutaraldehyde in AFFF/seawater mixtures, and thus do not provide a direct comparison of the effect of artificial vs. natural seawater on AFFF stability and surface tension. No significant changes were observed in DST for any of the AFFFs in the artificial seawater/glutaraldehyde between the unheated and aged samples. This indicates that either the increase observed for National Foam in the aging tests in natural seawater only happens in natural seawater, or (less likely) the glutaraldehyde affected the results.

FIRE TEST PERFORMANCE EVALUATIONS

Fire performance field evaluations using the AFFF Military Specification fire test protocols (pool fire extinguishment and burnback performance) were conducted for test protocol guidance. The fire performances of the half strength Type 6 AFFF mixtures were evaluated according to the MIL-F-24385F protocols for extinguishment and burnback with the 28 ft² pool test pan. National samples #2 (molybdate adduct only) and #3 (Dowacil 75 adduct only) were not tested following the poor performance of the National AFFF control (#1) and National with both adducts (#4). Results are given below:

Fire Extinguishment and Burnback Times - Aged Formulations (MilSpec MIL-F-24385F)

Agent	Extinguishment (MIL Spec max 45 Sec)	Burnback (MIL Spec min 300 sec)
3M Control	32	330
3M w/Adducts	34	333
Chemguard Control	35	533
Chemguard w/adducts	35	481
Ansul Control	43	542
Ansul w/adducts	66	419
National Control	57	450
National w/adducts	75	462

While the time results are compared to the performance times required by the AFFF specification, it this is for illustration only, as the conditions used are not the same as those used for the specification protocols (MIL-F-24385F does not include a half strength test of aged AFFF in salt water). As noted above, test conditions for this task were selected to be more stringent to better allow differentiation of any performance decrement. The significant comparison is the degree of performance decrement relative to the control tests.

Fire Test Performance and DST Correlations

Ansul and National foams showed decreased fire extinguishment performance compared with 3M and Chemguard products. Ansul and National AFFF performance decreased further with adducts. The performance of all National tested mixtures decreased markedly when aged in natural seawater. These fire test results correspond very well with dynamic surface tension results. DST is a valid predictor for fire extinguishment capability. Those mixtures whose DST exceeded 22 dynes/cm at a surface age of 10 seconds had significant increases in extinguishment times. Mixtures with 10 second DST values lower than 22 dynes/cm all had extinguishment times clustered in a narrow range from 32-35 seconds. Burnback properties (more dependent on foam resilience and resistance to radiant energy, not on film formation or spreading) do not correlate with DST, with all mixtures exceeding the minimum required burnback times.

CONCLUSIONS

Several approaches to mitigating H₂S formation from stagnant seawater / AFFF have been considered and eliminated. Antimicrobials offer an option without decreasing fire protection performance for at least one currently available Qualified Procurement List AFFF commercial product. Thus, if the mitigation techniques prove to be effective in mitigating H₂S production, there is an acceptable option available. NAVSEA is conducting antimicrobial effectiveness evaluations under realistic conditions using firemain and AFFF piping aboard inactive US Navy ships.

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REFERENCE

R. L. Tuve, H. B. Peterson, E. J. Jablonski, and R. R. Neill, "A New Vapor-Securing Agent for Flammable-Liquid Fire Extinguishment" Naval Research Laboratory Report #6957, March, 1964

B.A. Williams and R. S. Sheinson, "Environmental and Performance Issues in MilSpec AFFF" Proceedings of the Marine Environmental Engineering Technology Symposium (MEETS), Arlington, VA, August 21-22, 2003